RESEARCH PAPER

Performance of rice-hull-PE composite exposed to natural weathering

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Abstract: Rice-hull powder is widely used in manufacturing reinforced plastic composites. However, its weathering ability is rarely considered. We studied the performance of two types of rice-hull-polyethylene (RH-PE) composites after they were exposed outdoor to natural weathering for two years. The samples did not change in bending strength and elasticity modulus. At the end of the testing period, colour lightness had increased by more than 23% and total colour had changed by more than 9 units. This means the colour evidently differentiate from the original colour that the customers choose. The analyses of Fourier-transform infrared (FTIR) and X-ray photoelectron spectroscopy (XPS) showed that oxidation had occurred on sample surfaces. Red lumber presented an obvious C=O peak after weathering, while yellow lumber did not present an obvious peak as evidence of oxidation. Both types of lumbers showed a reduction of lignocellulosic groups and amorphous regions of PE.

Keywords: rice-hull; polyethylene; composites; weathering

Introduction

With rapid growth in the use of natural-fiber-reinforced polymer composites, people have become more concerned with their weathering ability. Changes of mechanical properties, colour and surface chemistry after weathering have been addressed by several research groups. Temperature, moisture, UV radiation, and fungi are all known to be the degrading factors for natural-fiber-reinforced polymer composites.

It has been shown that the colour of wood-plastic composites (WPCs) lightens after weathering (Falk et al. 2000; Matuana et al.

2001; Stark et al. 2004a; Muasher and Sain 2006). The amount and rate of lightening can vary depending upon manufacturing method, such as, exposure type and addition of a photostabilisation system. The manufacturing method directly influences the surface characteristics of WPCs and their response to weathering. Injection-molded composites lightened more slowly upon weathering than extruded composites, largely due to the hydrophobic character of the high-density-polyethylene (HDPE)-rich layer that formed on the surface of the composite during injection molding. This delayed some changes to the composite during weathering (Stark et al. 2004). The presence of moisture also greatly contributed to WPC lightening during weathering. The lightening of WPCs exposed to xenon-arc radiation with water spray was more evident than that of WPCs with xenon-arc radiation only (Stark 2006). Water accelerates oxidation reactions and causes wood fibers to swell, creating more openings for light penetration. In addition, water can remove some water-soluble extractives that impart colour to the wood particles.

Fourier-transform infrared (FTIR) spectroscopy is a useful tool for determining chemical changes at the surface of a composite. Peaks that appear in the spectra can be assigned to functional groups present at the composite surface. Thus, Oxidation at the degraded surface can be detected throughout weathering (Matuana et al. 2001; Muasher and Sain 2006; Stark et al. 2004a; Selde´n et al. 2004; Colom et al. 2000).

Most researches on weathering are conducted in accelerated UV weathering or xenon-arc weathering, because long-term observation of the weathering of WPCs outdoors is not sufficient to identify all the phenomena of interest. In addition, in North America, where WPC products have flourished, wood flour is generally used as the natural-fiber component. Pine, maple, and oak flours with mesh sizes between 20 and 100 mesh are commonly available for use in wood-plastic composites. Wood flour is typically incorporated into wood-plastic composites at 50%–60% by weight (Stark and Matuana 2007). However, in recent years, the use of greater quantities of agricultural plant fibers to reinforce polymers has become accepted as fact. For example, in China, many manufacturers use rice-hull powder as the fiber component because rice-hull powder is universally available and costs much less than wood fibers.

In this study, the properties and surface chemistry of two kinds

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of rice-hull-PE composites were evaluated after they were exposed outdoor to natural weathering for two years. The purpose of this research is to prove that rice-hull powder is a suitable resource for use in reinforced polymer composites and to investigate the degradation characteristics of this material by weathering with a view to improving its formulation.

Materials and methods

Materials

The materials used in these long-term tests were two kinds of extruded rice-hull-PE composite from a cooperating company; these products containing 50% rice hull powder were used for outdoor decks and rails. One lumber product had a solid cross-section and a red color and the size of lumber was 500 mm×140 mm×25 mm. The second lumber had a yellow color and the cross-sectional profile was shown in Fig. 1. The size of lumber was 650 mm×142 mm×35 mm.
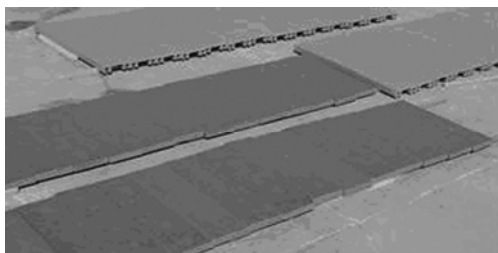

Fig. 1 Red lumber with solid cross-section and yellow lumber with a profiled cross-section

Weathering

Weathering was conducted on the roof of a building at Northeast Forestry University, Harbin city, Heilongjiang Province. The building is 20 m high and its roof is wide with no obstructions. Samples were placed horizontally on the roof and supported by two stickers. Two types of composites were exposed to the variable weather factors, such as, precipitation, snow, sunlight, temperature, moisture and wind. Mechanical properties, color changes, and surface properties of these specimens were measured after 5, 12, 17 and 24 months.

Harbin is located at longitude 125°42′E–130°10′E and latitude 44°04′N–46°40′N. It is a part of mild temperate zone with continental monsoon winds. In summer, the climate in Harbin is damp and hot with abundant rainfall, and light, heat, and rain effects can all be observed in the same season. Summer temperature varies averagely between 19.4°C and 22.4°C. In winter, the climate is cold and dry with an average temperature of about -14.2°C.

Mechanical properties

After weathering for the desired time period, six samples of each

type of lumber were harvested to test their bending properties. Bending tests in four-point loading were performed according to ASTM D7031-04, "Standard Guide for Evaluating Mechanical and Physical Properties of Wood-Plastic Composite Products". Load and deflection were continuously recorded until failure, and these data were used to calculate bending strength (BS) and modulus of elasticity (MOE). Loading rate was 12 mm·min^{-1} for red lumber and 15 mm·min^{-1} for yellow lumber. The ratio of span to thickness was 16:1.

Colour

The colour of exposed and unexposed specimens was measured with a NF 333 Photometer (Nippon Denshoku Company). Absolute chromaticity measurements were taken using the three-parameter CIE (International Commission on Illumination) scale: L*, a*, and b* system. The L* parameter is the lightness factor (amount of reflected light), while a* and b* are the chromaticity coordinates (chroma and hue respectively). L* provides a quantitative measure of the intensity of fading. A higher L* value indicates greater fading (higher reflectivity), (Falk et al. 2000). In addition, the total colour difference (ΔE) was calculated. ΔE is the square root of the sum of the squares of the differences of chromaticity coordinates:

$$\Delta E = [(\Delta a)^2 + (\Delta b)^2 + (\Delta L)^2]^{1/2} \tag{1}$$

where, ΔE is the total colour difference; Δa, Δb and ΔL are the difference between the value before and after exposed to weathering, respectively.

Fourier-transform infrared spectroscopy

Fourier-transform infrared (FTIR) spectroscopy was conducted on a MAGNA – IR560 (NICOLE) spectrometer to provide information about functional groups present at the composite surface before and after weathering. For each sample, scans were recorded in transparency units from 4000 cm^{-1} to 400 cm^{-1}. An index is often used to detect changes in chemical functional groups, such as the carbonyl index calculated by Stark and Matuana (2004b) using the following equation:

$$C = I\,1715/I\,2912 \tag{2}$$

where, C is the Carbonyl index. I represents the peak intensity. Peak intensity was normalised using the peak at 2912 cm^{-1}, which corresponds to alkane CH stretching vibrations of methylene groups (-CH2-), (Stark and Matuana 2007). This peak was used as a reference peak because it changed minimally during weathering.

X-ray photoelectron spectroscopy (XPS)

X-ray photoelectron spectra were generated using a K-Alpha spectrograph (Thermo Scientific). To determine the types of oxygen-carbon bonds present, chemical bond analysis of carbon

was accomplished by fitting a curve to the C1s peak and deconvoluting it into four subpeaks (C1, C2, C3 and C4). The resulting deconvoluted peak assignments with their corresponding binding energies and bond types are shown in Table 1. An oxidized to unoxidized carbon ratio ($C_{ox/unox}$) was calculated using Eq.(Stark and matuana 2007):

$$C_{ox/unox} = C_{oxidized}/C_{unoxidized} = (C_2+C_3+C_4)/C_1 \qquad (3)$$

where, C_1, C_2, C_3 and C_4 are four subpeaks respectively.

Table 1. Deconvoluted peak assignments with corresponding binding energies and bond types for XPS scan of C$_{1s}$

Carbon group	Binding energy (eV)	Bond
C1	283	C-C or C-H
C2	284.5	C-O
C3	286	O-C-O or C=O
C4	287.5	O-C=O

Results and analysis

Changes in flexural properties

Both red and yellow lumber showed small decreasing trend in flexural properties in the first 12 months (Table 2). However, at the end of the testing period, after 24 months, increases were observed in both bending strength (BS) and modulus of elasticity (MOE). This is considered to be due to the dead weight of the lumber. After sitting outside for a long time, the lumber samples bended downward (Fig. 2) because of their dead weight. In other words, the lumber underwent creep. During test period, the upper weathered surfaces were exposed to tension forces and the bottom surfaces were exposed to compression forces. This resulted in more resistance to breaking force. The results also showed that red lumber increased more in flexural properties than did yellow lumber. Because the red lumber had a solid structure, which gave dead weight larger than the yellow lumber, the lumber bended more seriously. Although the rice-hull-PE composite did not bear load, its dead weight would be sufficient to result in bending. Although the rice-hull-PE composite used in these tests does not have satisfactory mechanical properties, rice hulls are an abundant and easily available resource. Many manufacturers use them to reduce cost but do not use additives such as coupling agents to improve strength. This practice gives researchers a good opportunity to develop better processing methods that are suitable for using rice hulls in plastic composites.

Fig. 2 Deformation of red lumber after outdoor weathering for 24 months

Table 2. Flexural properties of rice-hull-PE composites after exposed to weathering

Weathering time (months)	Red lumber		Yellow lumber	
	BS (MPa)	MOE (GPa)	BS (MPa)	MOE (GPa)
0	13.65 (0.29)	1.77 (0.22)	11.94 (0.96)	1.09 (0.20)
5	13.10 (0.78)	1.72 (0.30)	11.60 (0.56)	1.05 (0.13)
12	13.07 (1.68)	1.62 (0.22)	12.01 (0.55)	1.10 (0.07)
17	13.89 (2.01)	1.73 (0.22)	12.04 (0.59)	1.09 (0.06)
24	15.83 (2.59)	2.20 (0.16)	13.94 (1.23)	1.31 (0.19)

Notes: BS is bending strength; MOE is modulus of elasticity.

Changes in colour

The red lumber and yellow lumber exhibited the same trends in fading (Fig. 3). After natural weathering for two years, their lightness increased by 26.2% and 23.7% respectively. The fading of the red lumber and yellow lumber continued over the two years. For red lumber, the fading was very slow or almost non-existent in winter (months 0–5 and 12–17), and faster in summer (months 5–12 and 17–24). This was probably due to stronger sunlight and rainfall in summer. However, the yellow lumber faded continuously after the initial five months of exposure, including during the second winter. Rice-hull-PE composites experienced significant fading over the two years and seemed to fade continuously.
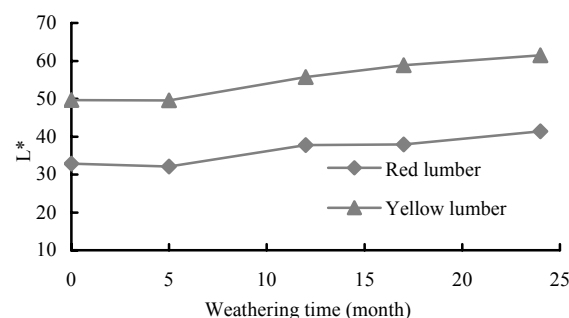

Fig. 3 Lightness of the surfaces of red and yellow lumber samples after varying periods of weathering

Besides fading, colour change is another problem experienced during weathering. The total colour change, as shown in Fig. 4, results in a colour much different from the initial value. The colour of yellow lumber changed more than that of red lumber (Fig. 4). At the end of the second year, the colour of the yellow lumber had changed by 12.8 units, while that of the red lumber had changed by 9.2 units.

From the observed values of a* and b* in prior research, it can be seen that the yellow lumber experienced dramatic losses of yellow tone and red tone over the first summer, then these values remained stable. However, the yellow lumber continued to fade in the whole year, resulting in a larger overall colour change. As for red lumber, its colour-change behavior varied more with the season; L, a*, and b* all changed more in summer and stable in winter.
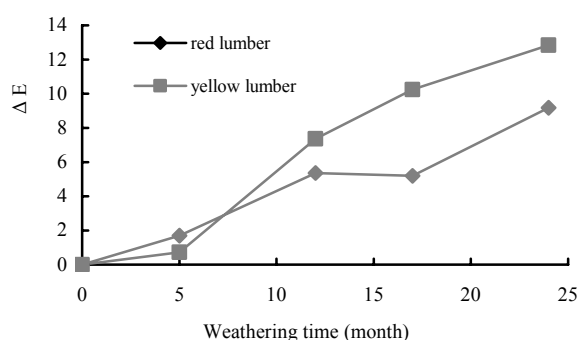
Fig. 4 Total colour changes on the surfaces of red and yellow lumber after varying periods of weathering

For bio-fiber-reinforced plastic products, fading after natural weathering is an obvious characteristic that people notice. This research has indicated that colour may also change and become very different from that initially designed. It has long been recognized that wood-plastic composites fade with time. This is an undeniable characteristic of bio-fiber-reinforced plastic composites. Nowadays, almost all informational and marketing materials from manufacturers, as well as their warranty policies, contain an acknowledgement that their products fade under exposure to sunlight. However, this acknowledgement is often vague and elusive and is sometimes even used as a marketing tool, with claims that the fading of deck boards is a good and esthetically sound feature (Klyosov 2007). Although most manufacturers state that the weathering process will halt after several months, this claim is dubious. This research indicated that fading or colour change of samples may continue over a longer time.

Surface chemical changes

The broad peak in the 3230–3550 cm^{-1} band is associated with mixed hydroxyl groups originating mainly from cellulose. The peaks around 1 632 cm^{-1} and 1 070 cm^{-1} are characteristic peaks associated with the lignin and cellulose components, respectively (Fig. 5). The peaks at 2 800–3 000 cm^{-1}, 1 470 cm^{-1}, and 710 cm^{-1} are due to alkane C-H stretching of methylene, which appear as very strong peaks in HDPE.

The FTIR spectrum of rice-hull powder was compared with that of the weathered fiber component in rice-hull-PE composites. FTIR spectra were obtained for weathered and unweathered rice-hull-PE composites (Fig. 6 and 7). Wood and carbonyl indices are listed in Table 3. After weathering for 24 months, it can be seen that hydroxyl groups at the surface of two kind lumbers decreased significantly based on the decrease in the broad peak around 3 400 cm^{-1} and the weakened peak at 1 070 cm^{-1}. For red lumber the peak at 1 640 cm^{-1} almost disappeared after weathering, while, there's a smaller change for yellow lumber at this position.

It is worth noting that the increase in the carbonyl group (C=O) absorbance at 1 730 cm^{-1} for red lumber samples is accompanied by a dramatic decrease in the aromatic C=C band at 1632 cm^{-1} in Fig. 6. The disappearance of the peak at 1632 cm^{-1} indicated that

the lignin aromatic structure was being degraded and that it is very likely that the lignin aromatic structure is being degraded and further oxidized to form paraquinone chromophores. On the other hand, in the yellow lumber sample, the peaks around 1 230 cm^{-1} of an ether (C-O-C) or at 1 730 cm^{-1} are not clearly seen, even though accompanied by a significant reduction of the peak at 1 050 cm^{-1}. It is assumed that the peak at 1 230 cm^{-1} was disturbed by the broad peak around 1 050 cm^{-1}, and that the presence of oxygen cannot be confirmed.
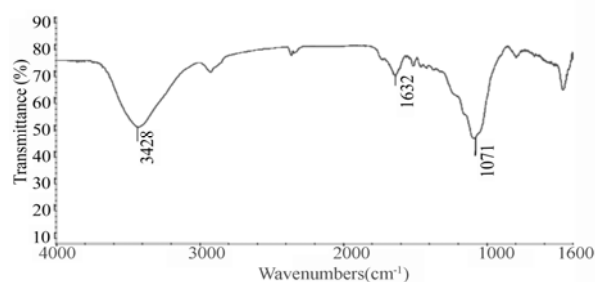

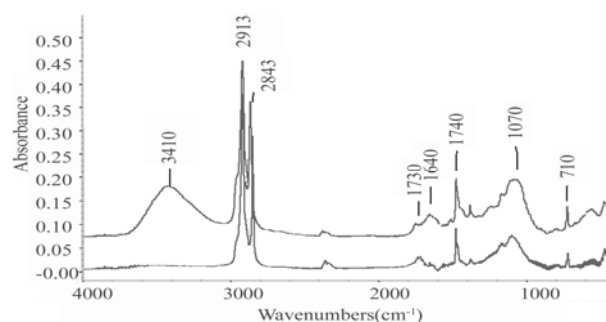**Fig. 5 FTIR spectrum of rice-hull powder**

Fig. 6 FTIR spectrum of naturally weathered (down) and unweathered (up) red lumber
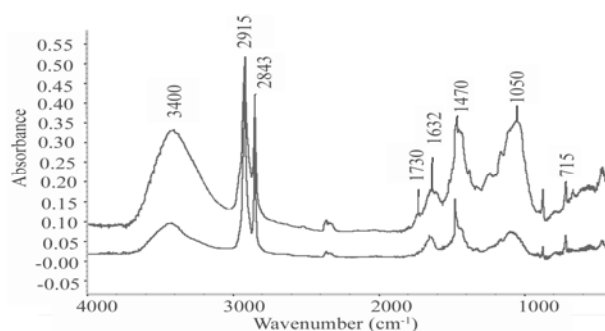

Fig. 7 FTIR spectrum of naturally weathered (down) and unweathered (up) yellow lumber

The photodegradation of wood can be attributed to the degradation of its components, namely cellulose, hemicellulose, lignin and extractives. However, the research has shown that the breakdown of lignin to water-soluble products, which eventually leads to the formation of chromophoric functional groups such as carboxylic acids, quinones, and hydroperoxy radicals, is the main

cause of discoloration, mainly yellowing in wood (Heitner 1993; Hon 2001). Lignin undergoes photodegradation by many different pathways. One of the most frequently proposed reaction pathways is the Phenoxy Quinone Redox Cycle (Castellan et al. 1993; Ragauskas 1993; Zhang and Gellerstedt 1998; Li and Raguausdas 2000). This reaction suggests that the hydroquinones and paraquinones are a redox couple. Under irradiation, the changing process begins with the oxidation of the hydroquinones to form paraquinones (chromophoric structures) that are further reduced to hydroquinones as the cycle repeats itself (Muasher and Sain 2006).

Table 3. Wavenumbers with their corresponding functional groups, vibrational peaks and indices

Wavelength (cm^{-1})	Functional group	Vibrational type	Index of red lumber		Index of yellow lumber	
			Unweathered	Weathered	Unweathered	Weathered
2913 or 2915	-CH$_2$-	C-H stretching				
1730	R(C=O)OH	C=O stretching	0.079	0.088		
1632 or 1640	C=C	Aromatic C=C stretching	0.183	0.019	0.186	0.158
1470	-CH$_2$-	C-H scissor vibration	0.565	0.335	0.656	0.469
1050 or 1070	RCH$_2$-OH	C-O stretching	0.640	0.270	0.765	0.218
710 or 715	-CH$_2$-	C-H rocking, amorphous	0.280	0.078	0.233	0.180

The decreasing in characteristic peaks of PE (at 1470 cm^{-1} and 710 cm^{-1}) also can be seen. Red lumber decreased more than yellow lumber, almost as obviously as that of lignocellulosic material. This may indicate that the PE matrix of yellow lumber degraded less than the rice hull enclosed in it and had less effect on the colour change.

FTIR was also used to determine the change in crystallinity of HDPE before and after weathering. Some researchers have calculated crystallinity using the doublet peaks at 730 cm^{-1} and 720 cm^{-1} (Stark and Matuana 2004b; Muasher and Sain 2006). The peaks at 1474 cm^{-1} and 730 cm^{-1} correspond to the polyethylene crystalline content, and the peaks at 1464 cm^{-1} and 720 cm^{-1} represent the amorphous content. In this research, an obvious double peak around 730 cm^{-1} was not identified. However, the peak around 710 cm^{-1} corresponding to the polyethylene amorphous content decreased and more significantly at the surface of red lumber, which means that the amorphous region decreased.

In the two types of composites, the red lumber deformed, lightened and surface chemically changed more severely than the yellow lumber. The degradation reaction of the lignin resulted in final products with C=O, which lightened the color of the composite. And PE component also degraded after experiencing two year weathering.

Table 4. Relative quantities of various carbon-oxygen bonds in the red lumber sample surface by XPS

Treatment	C1	C2	C3	C4
Unweathered	83.04	4.54	2.3	2.97
Weathered for 17 months	81.47	4.69	3.04	2.15

The main elements detected using XPS were oxygen and carbon. The C$_{1s}$ region was deconvoluted into four subpeaks, C1, C2, C3, and C4. Deconvolution of the carbon peak showed that the relative amount of the C1 carbon group, representing a C-C or C-H bond, decreased after weathering (Table 4). The C1 peak did not have a carbon–oxygen bond, whereas C2, C3, and C4 all possess a carbon–oxygen bond. A decrease in the C1 peak indicates a decreased concentration of unoxidised carbon atoms. On the other hand, increases in C2 and C3 were observed. The C$_{oxidized}$/C$_{unoxidized}$ ratio increased from 0.118 before weathering to 0.121 after weathering for 17 months, which imply that surface oxidation occurred.

Stark and Matuana (2004) found that surface oxidation due to weathering was more pronounced for wood-fiber (WF)/HDPE composite samples than for pure HDPE samples. The Cox/unox ratio increased dramatically for WF/HDPE composites after weathering (an 80% increase compared with a 5% increase for pure HDPE samples), which suggests that the addition of WF to the HDPE matrix exacerbates the photo-oxidation of the sample surface. As shown by FTIR analysis, the main functional group changed in the rice hulls. It can be assumed that the main oxygen reaction resulted from bio-based components. In the present research, only a small increase was observed in C2, with the main increase occurring in C3 and a decrease in C4. These results are different from those reported by Stark and Matuana (2004b), who found the increase in the Cox/unox ratio to be due mainly to an increase in hydroxyl groups (i.e., an increase in C2). This may be due to the difference in chemical composition between the rice hulls used in the current research and the wood used by Stark and Matuana (2004b). In addition, the Cox/unox ratio of RH/PE composites in this research was observed to increase by 12.5%, if C2 and C3 were only considered, this value was less than the increase observed by Stark and Matuana (2004b) for WF/HDPE composite. This may indicate that the accelerated weathering has a more dramatic effect than natural weathering and that simulated radiation results in different oxidation process.

Conclusion

Based on detailed observations and analysis for samples over 24 months, the authors have gained a greater insight into the degradation of rice-hull-PE composites. Solid lumber experienced more bending due to its greater dead weight. Although the BS and MOE did not change, significant fading and color change occurred in two types of lumber and appeared to continue for a

long time. The analysis of FTIR and XPS indicated that the rice-hull powder degraded more than the PE matrix. Oxygen was observed in the C=O present at one lumber surface. The rice-hull components of the surfaces were obviously degraded.

Rice hulls have been introduced into the WPC industry as an agriculture residue resource, which is a good way to increase their value and reduce the requirement for wood resources. Further research needs to address ways to improve the mechanical properties of rice-hull materials and inhibit color change in composites made from these materials.

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